

Patent B2

1 WHAT IS CLAIMED IS:

1. A product comprising a substrate to which is chemically bonded a monolayer of silicon atoms which are connected to other silicon atoms in said monolayer through oxygen atoms in said monolayer, wherein the monolayer is substituted with first and second hydrocarbyl substituents and each of the silicon atoms in said monolayer is substituted with said first hydrocarbyl substituent or said second hydrocarbyl substituent, wherein said first hydrocarbyl substituent is longer than said second hydrocarbyl substituent.

2. The product of Claim 1 wherein said first and second hydrocarbyl substituents are distributed essentially uniformly on said substrate.

3. The product of Claim 1 wherein said first hydrocarbyl substituent is selected from the group consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 60 carbon atoms, epoxide, and derivatives of alkyl or monounsaturated alkylene which contain a total of up to 60 carbon atoms and which contain one or more hetero linkages selected from the group consisting of -O-, -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-, -C(O)N(R)-, or -N(R)C(O)-; wherein the phenyl, alkyl, and alkylene are optionally substituted with one or more substituents selected from the group consisting of hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R), straight or branched alkyl containing 1 to 6 carbon atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹ and R² are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

1 4. The product of Claim 1 wherein said
second hydrocarbyl substituent is selected from the
group consisting of phenyl, alkyl containing 1 to 60
carbon atoms, monounsaturated alkylene containing 2 to
5 60 carbon atoms, epoxide, and derivatives of alkyl or
monounsaturated alkylene which contain a total of up to
60 carbon atoms and which contain one or more hetero
linkages selected from the group consisting of -O-,
-N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
10 -C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl
and alkylene are optionally substituted with one or more
substituents selected from the group consisting of
hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
straight or branched alkyl containing 1 to 6 carbon
15 atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
and R² are alkyl, alkoxy or alkylene containing up to 6
carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms.

5. The product of Claim 1 wherein the mole
ratio of said first hydrocarbyl substituent to said
20 second hydrocarbyl substituent on said substrate is
100:1 to 1:100.

6. A product according to Claim 1 wherein
the surface of said substrate comprises an inorganic
25 element or an oxide thereof, which is capable of forming
a bond to silicon atoms in said monolayer.

7. A product according to Claim 6 wherein
said inorganic element is selected from the group
consisting of Si, Al, Zr, P, Be, Mg, Ti, Al, V, Cr, Mn,
30 Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Nb, Mo, Ru,
Rh, Pt, Au, Ag, Tl, Pb and Bi.

B 1 6. A product according to Claim 5 wherein
the surface of said substrate comprises Al. 1

B 2 7. A product according to Claim 6 wherein
the surface of said substrate comprises Be. 1

B 5 8. A product according to Claim 8 wherein
the surface of said substrate comprises Ti. 1

B 11.9 A product according to Claim 8 wherein
the surface of said substrate comprises Zr. 9

10 12.10 A product according to Claim 11 wherein
said first hydrocarbyl substituent has the formula
 $\text{HOCH}_2\text{-CH(OH)CH}_2\text{-}$.

13.11 A product according to Claim 1 wherein
said substrate is bonded to the silicon atoms in said
monolayer through oxygen atoms.

15 14. A product according to Claim 1 comprising
silica gel to which is chemically bonded a protective
monolayer of silicon atoms which are connected to other
silicon atoms in said monolayer through oxygen atoms in
said monolayer, wherein the monolayer is substituted
20 with first and second hydrocarbyl substituents and each
of the silicon atoms in said monolayer is substituted
with said first hydrocarbyl substituent or said second
hydrocarbyl substituent, wherein said first hydrocarbyl
substituent is longer than said second hydrocarbyl
25 substituent.

15. The product of Claim 14 wherein said
first and second hydrocarbyl substituents are
distributed essentially uniformly on said substrate.

16. The product of Claim 14 wherein said
30 first hydrocarbyl substituent is selected from the group
consisting of phenyl, alkyl containing 1 to 60 carbon
atoms, monounsaturated alkylene containing 2 to 60

1 carbon atoms, epoxide, and derivatives of alkyl or
monounsaturated alkylene which contain a total of up to
60 carbon atoms and which contain one or more hetero
linkages selected from the group of consisting of -O-,
5 -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
-C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl
and alkylene are optionally substituted with one or more
substituents selected from the group consisting of
hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
10 straight or branched alkyl containing 1 to 6 carbon
atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
and R² are alkyl, alkoxy or alkylene containing up to 6
carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms.

15 17. The product of Claim 14 wherein said
first hydrocarbyl substituent is selected from the group
consisting of phenyl, alkyl containing 1 to 60 carbon
atoms, monounsaturated alkylene containing 2 to 60
carbon atoms, epoxide, and derivatives of alkyl or
20 monounsaturated alkylene containing a total of up to 60
carbon atoms and which contain one or more hetero
linkages selected from the group of consisting of -O-,
-N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
-C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl
25 and alkylene are optionally substituted with one or more
substituents selected from the group consisting of
hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
straight or branched alkyl containing 1 to 6 carbon
atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
30 and R² are alkyl, alkoxy or alkylene containing up to 6
carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms.

1 18. The product of Claim 14 wherein the mole
ratio of said first hydrocarbyl substituent to said
second hydrocarbyl substituent on said substrate is
100:1 to 1:100.

5 19. The product of Claim 14 wherein said
first hydrocarbyl substituent contains 2 to 24 carbon
atoms.

10 20. The product of Claim 14 wherein said
second hydrocarbyl substituent contains 1 to 6 carbon
atoms.

15 21. The product of Claim 14 wherein said
first hydrocarbyl substituent is octadecyl and said
second hydrocarbyl substituent is propyl.

20 22. The product of Claim 14 wherein said
first hydrocarbyl substituent is octadecyl and said
second hydrocarbyl substituent is methyl.

25 23. The product of Claim 14 wherein said
first hydrocarbyl substituent is octyl and said second
hydrocarbyl substituent is methyl.

30 24. The product of Claim 14 wherein said
first hydrocarbyl substituent is butyl and said second
hydrocarbyl substituent is methyl.

35 25. The product of Claim 14 wherein said
first hydrocarbyl substituent occupies about 20 to about
50% of the surface of said substrate.

40 26. The product of Claim 14 wherein the mole
ratio of said first hydrocarbyl substituent to said
second hydrocarbyl substituent is about 1:1 to about
1:4.

45 27. In the method of chromatographically
separating a mixture of substances using a chromato-

1 graphic material, the improvement wherein said material
B is a product according to Claim 8.

28. In the method of chromatographically
separating a mixture of substances using a chromato-
5 graphic material, the improvement wherein said material
is a product according to Claim 7.

29. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
10 is a product according to Claim 14.

30. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
is a product according to Claim 15.

15 31. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
is a product according to Claim 16.

32. In the method of chromatographically
20 separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
is a product according to Claim 17.

33. In the method of chromatographically
separating a mixture of substances using a chromato-
25 graphic material, the improvement wherein said material
is a product according to Claim 18.

34. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
30 is a product according to Claim 19.

35. In the method of chromatographically
separating a mixture of substances using a chromato-

1 graphic material, the improvement wherein said material
is a product according to Claim 20.

36. In the method of chromatographically
separating a mixture of substances using a chromato-
5 graphic material, the improvement wherein said material
is a product according to Claim 21.

37. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
10 is a product according to Claim 25.

38. In the method of chromatographically
separating a mixture of substances using a chromato-
graphic material, the improvement wherein said material
is a product according to Claim 26.

15 39. A product according to Claim 1 comprising
a glass surface to which is chemically bonded a
protective monolayer of silicon atoms which are
connected to other silicon atoms in said monolayer
through oxygen atoms in said monolayer, wherein the
20 monolayer is substituted with first and second
hydrocarbyl substituents and each of the silicon atoms
in said monolayer is substituted with a first
hydrocarbyl substituent or a second hydrocarbyl
substituent, wherein said first hydrocarbyl substituent
25 is longer than said second hydrocarbyl substituent.

40. The product of Claim 39 wherein said
first and second hydrocarbyl substituents are
distributed essentially uniformly on said substrate.

41. The product of Claim 39 wherein said
30 first hydrocarbyl substituent is selected from the group
consisting of phenyl, alkyl containing 1 to 60 carbon
atoms, monounsaturated alkylene containing 2 to 60

1 carbon atoms, epoxide, and derivatives of alkyl or monounsaturated alkylene which contain a total of up to 60 carbon atoms and which contain one or more hetero linkages selected from the group of consisting of -O-,
5 -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-, -C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl and alkylene are optionally substituted with one or more substituents selected from the group consisting of hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
10 straight or branched alkyl containing 1 to 6 carbon atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹ and R² are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

15 42. The product of Claim 39 wherein said second hydrocarbyl substituent is selected from the group consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 60 carbon atoms, epoxide, and derivatives of alkyl or
20 monounsaturated alkylene containing a total of up to 60 carbon atoms and which contain one or more hetero linkages selected from the group of consisting of -O-, -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-, -C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl and alkylene are optionally substituted with one or more substituents selected from the group consisting of hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R), straight or branched alkyl containing 1 to 6 carbon atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
25 and R² are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

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1 43. The product of Claim 39 wherein the mole
ratio of said first hydrocarbyl substituent to said
second hydrocarbyl substituent on said substrate is
100:1 to 1:100.

5 44. The product of Claim 39 wherein said
first hydrocarbyl substituent contains 2 to 24 carbon
atoms.

10 45. The product of Claim 39 wherein said
second hydrocarbyl substituent contains 1 to 6 carbon
atoms.

46. The product of Claim 39 wherein said
first hydrocarbyl substituent is octadecyl and said
second hydrocarbyl substituent is propyl.

15 47. The product of Claim 39 wherein said
first hydrocarbyl substituent occupies about 20 to about
50% of the surface of said substrate.

20 48. The product of Claim 39 wherein the mole
ratio of said first hydrocarbyl substituent to said
second hydrocarbyl substituent is about 1:1 to about
1:4.

25 49. The method of rendering a surface
resistant to chemical and mechanical degradation which
comprises forming on said surface a protective monolayer
of silicon atoms which are connected to other silicon
atoms in said monolayer through oxygen atoms in said
monolayer, wherein the monolayer is substituted with
first and second hydrocarbyl substituents and each of
the silicon atoms in said monolayer is substituted with
a first hydrocarbyl substituent or a second hydrocarbyl
30 substituent, wherein said first hydrocarbyl substituent
is longer than said second hydrocarbyl substituent.

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1 50. The method of Claim 49 wherein said first hydrocarbyl substituent is selected from the group consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 60 5 carbon atoms, epoxide, and derivatives of alkyl or monounsaturated alkylene which contain a total of up to 60 carbon atoms and which contain one or more hetero linkages selected from the group consisting of -O-, -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-, -C(O)N(R)-, or -N(R)C(O)-; wherein the phenyl, alkyl, and alkylene are optionally substituted with one or more substituents selected from the group consisting of hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R), straight or branched alkyl containing 1 to 6 carbon 15 atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹ and R² are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

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51 15. The method of Claim 49 wherein said 20 second hydrocarbyl substituent is selected from the group consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 60 carbon atoms, epoxide and derivatives of alkyl or monounsaturated alkylene which contain a total of up to 60 carbon atoms and which contain one or more hetero linkages selected from the group consisting of -O-, -N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-, -C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl and alkylene are optionally substituted with one or more 25 substituents selected from the group consisting of hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R), straight or branched alkyl containing 1 to 6 carbon 30 atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹ and R² are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

1 atoms, and $-R^1Si(R^2)_{3-n}(OH)_n$ wherein n is 1, 2 or 3, R^1 and R^2 are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or alkyl containing 1 to 6 carbon atoms.

5 52. The method according to Claim 49 wherein material having a glass surface is rendered resistant to chemical and mechanical degradation of said surface.

53. The method of Claim 52 wherein said first hydrocarbyl substituent is selected from the group 10 consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 60 carbon atoms, epoxide, and derivatives of alkyl or monounsaturated alkylene which contain a total of up to 60 carbon atoms and which contain one or more hetero 15 linkages selected from the group consisting of $-O-$, $-N(R)-$, $-S-$, $-C(O)-$, $-SO_2-$, $-C(O)O-$, $-OC(O)-$, $-C(O)N(R)-$, or $-N(R)C(O)-$; wherein the phenyl, alkyl, and alkylene are optionally substituted with one or more substituents selected from the group consisting of 20 hydroxyl, halogen, cyano, nitro, $-COOH$, $-SO_3H$, $-N(R)(R)$, straight or branched alkyl containing 1 to 6 carbon atoms, and $-R^1Si(R^2)_{3-n}(OH)_n$ wherein n is 1, 2 or 3, R^1 and R^2 are alkyl, alkoxy or alkylene containing up to 6 carbon atoms, and R in each occurrence is hydrogen or 25 alkyl containing 1 to 6 carbon atoms.

54. The method of Claim 52 wherein said second hydrocarbyl substituent is selected from the group consisting of phenyl, alkyl containing 1 to 60 carbon atoms, monounsaturated alkylene containing 2 to 30 60 carbon atoms, epoxide, and derivatives of alkyl or monounsaturated alkylene which contain a total of up to

1 60 carbon atoms and which contain one or more hetero
linkages selected from the group consisting of -O-,
-N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
-C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl
5 and alkylene are optionally substituted with one or more
substituents selected from the group consisting of
hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
straight or branched alkyl containing 1 to 6 carbon
atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
10 and R² are alkyl, alkoxy or alkylene containing up to 6
carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms.

55. The method of Claim 52 wherein said
material is selected from the group consisting of
15 glassware, optical fiber, and capillaries.

56. The method of Claim 55 wherein said
material is a fiber optic filament.

57. The method of Claim 49 wherein material
having a silica gel surface is rendered resistant to
20 chemical and physical degradation of said surface.

58. The method of Claim 57 wherein said first
hydrocarbyl substituent is selected from the group
consisting of phenyl, alkyl containing 1 to 60 carbon
atoms, monounsaturated alkylene containing 2 to 60
25 carbon atoms, epoxide and derivatives of alkyl or
monounsaturated alkylene which contain a total of up to
60 carbon atoms and which contain one or more hetero
linkages selected from the group consisting of -O-,
-N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
30 -C(O)N(R)-, or -N(R)C(O)-; wherein the phenyl, alkyl,
and alkylene are optionally substituted with one or more
substituents selected from the group consisting of

1 hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
straight or branched alkyl containing 1 to 6 carbon
atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
and R² are alkyl, alkoxy or alkylene containing up to 6
5 carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms, and R in each
occurrence is hydrogen or alkyl containing 1 to 6 carbon
atoms.

59. The method of Claim 57 wherein said
10 second hydrocarbyl substituent is selected from the
group consisting of phenyl, alkyl containing 1 to 60
carbon atoms, monounsaturated alkylene containing 2 to
60 carbon atoms, epoxide, and derivatives of alkyl or
monounsaturated alkylene which contain a total of up to
15 60 carbon atoms and which contain one or more hetero
linkages selected from the group consisting of -O-,
-N(R)-, -S-, -C(O)-, -SO₂-, -C(O)O-, -OC(O)-,
-C(O)N(R)-, and -N(R)C(O)-; wherein the phenyl, alkyl
and alkylene are optionally substituted with one or more
20 substituents selected from the group consisting of
hydroxyl, halogen, cyano, nitro, -COOH, -SO₃H, -N(R)(R),
straight or branched alkyl containing 1 to 6 carbon
atoms, and -R¹Si(R²)_{3-n}(OH)_n wherein n is 1, 2 or 3, R¹
and R² are alkyl, alkoxy or alkylene containing up to 6
25 carbon atoms, and R in each occurrence is hydrogen or
alkyl containing 1 to 6 carbon atoms.

60. A method for treating the surface of an
article comprising contacting said surface with silanes
of the formula R¹SiX₃ and R²SiX₃, wherein R¹ and R² are
30 hydrocarbyl substituents and X is a leaving group,
provided that R¹ is longer than R², under conditions
whereunder said silanes react at said surface and form a

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1 monolayer of silicon atoms chemically bonded to said
surface which silicon atoms are connected to other
silicon atoms in said monolayer through oxygen atoms in
said monolayer, wherein each of said silicon atoms in
5 said monolayer is substituted with R¹ or R².

62/7 The method according to Claim 60¹⁶ which
comprises contacting said surface with said silanes in a
solution of said silanes.

10 62/8 The method according to Claim 60¹⁶ which
comprises contacting said surface of said article with a
gas comprising said silanes.

15 62/9 A method according to Claim 62¹⁸ wherein
said article is a fiber optic filament, the method
comprising drawing said filament through said gas under
conditions whereunder said silanes react with the
surface of said filament.

20 64. A method for treating a surface
comprising silicon and oxygen atoms, said surface
comprising hydroxyl substituents, to remove said
hydroxyl substituents, comprising:

(a) converting said hydroxyl
substituents to halide substituents, and then
(b) converting said halide substituents
to alkyl groups containing 1 to 6 carbon atoms.

25 65. The method of Claim 64 wherein said
halide is chloride.

30 66. The method of Claim 65 wherein said
hydroxyl substituents are converted to chloride by
reacting said hydroxyl substituents with thionyl
chloride.

1 67. The method of Claim 66 wherein said
chloride is converted to alkyl groups by reacting the
product of step (a) with a Grignard reagent.

5 68. The method of Claim 67 wherein said
Grignard reagent has the formula (Alk)MgBr wherein Alk
signifies alkyl containing 1 to 6 carbon atoms.

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